

# PATENT SPECIFICATION

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## (54) MANUFACTURE OF ACRYLIC ACID

(71) We, BADISCHE ANILIN- & SODA - FABRIK AKTIENGESELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the manufacture of acrylic acid by oxidation of propylene in two stages via acrolein as intermediate, using oxidic catalysts.

It is known to oxidize propylene to acrylic acid in the gas phase in the presence of molecular oxygen-containing gases and steam and at an elevated temperature in contact with solid catalysts in two stages. In the first stage, the propylene is mainly converted to acrolein, and the resulting gas mixture is passed to the second stage without separation of the acrolein, where it is oxidized to acrylic acid in contact with a second catalyst.

Catalyst systems already proposed for the first stage contain elements in groups IVa to VIa, VIII and IVb to VIIb. Of these catalyst systems, tellurium - containing catalysts (catalysts containing tellurium dioxide or telluric acid or catalysts which contain bismuth or antimony with or without phosphorus) are distinguished by their particularly high selectivity in the formation of acrolein at a relatively low temperature of the saltpetre bath usually used for this reaction. Other suitable catalysts include those containing oxides of molybdenum, tungsten and tellurium or the oxides of cobalt, molybdenum and tellurium. Other catalysts which have been proposed contain, for example, iron, tin, antimony, vanadium, or nickel, cobalt, iron, bismuth, phosphorus and molybdenum in addition to oxygen, optionally with additions of samarium oxide and tantalum oxide. The manufacture and use of the first mentioned catalyst systems for the oxidation of propylene to acrolein is described, for example, in British Patents 1,193,489 and 1,243,794.

Catalysts which have been found satisfactory for use in the second stage are also oxidic catalysts in the aforementioned groups but with the restriction that generally no elements in groups Va and VIa may be used, and in particular no or only very little selenium or tellurium may be used, in order that the acrolein may be further oxidized to acrylic acid as completely as possible. Known catalysts contain, for example, cobalt and molybdenum or molybdenum, tungsten and vanadium, or tin, antimony and molybdenum in addition to oxygen.

It is advantageous to use catalysts which contain, in addition to oxygen, molybdenum, tungsten and iron and/or nickel and/or manganese and/or copper and, optionally, vanadium. The manufacture of these catalysts and their use in the oxidation of acrolein to acrylic acid is described in British Patent 1,213,325 and Canadian Patent 868,940.

The ultimate object of the teachings given in said literature is to obtain acrylic acid in an absolute yield which is as high as possible on the propylene introduced, whilst other factors of significance in carrying out these processes are not considered to a desirable extent.

One of the most important criteria is the space-time yield and the concentration of the acrylic acid in the condensate obtained. Considerable difficulties have been encountered in attempts to obtain high space-time yields and high condensate concentrations in industrial apparatus. Industrial single-stage or multistage processes for the synthesis of acrylic acid by gas-phase oxidation in the prior art are only capable of removing the locally occurring heat of reaction with the rapidity necessary for high conversions in a single pass when very uneconomical measures are adopted. For example, it is necessary to use tubes of narrow cross-section or to operate at low temperatures and thus with small amounts of catalyst and low throughputs (linear gas velocities) and, moreover, the gas to be oxidized must be protected from explosive combustion at the catalysts or

at least from overoxidation leading to undesirable by-products by dilution with large amounts of steam (up to 40% by volume). Relatively good absolute yields of acrylic acid, which may be as high as 50% of theory or more based on propylene introduced, are obtained, but an uneconomically high energy input and high investment costs are incurred because it is necessary to use low space velocities (long residence times) and the resulting acrylic acid is obtained in very dilute aqueous solution.

It has thus been desirable to make the entire process more economical by improving the space-time yield whilst having recourse to the previously worked-out methods of obtaining high absolute yields in a single pass. The present invention seeks to provide a safe oxidation process in which over-oxidation of the kind mentioned above is minimized and explosive combustion processes are reliably obviated.

According to the present invention there is provided a process for the manufacture of acrylic acid by two-stage oxidation of propylene with molecular oxygen in admixture with inert diluting gas in reaction tubes packed with catalyst, propylene being substantially oxidized to acrolein in the first stage and further oxidation to acrylic acid occurring in the second stage, the initial propylene concentration being above 2% molar based on the initial gaseous mixture and the rate of flow of the propylene or acrolein (as the case may be) supplied to each stage being greater than 60 liters per hour per liter of catalyst in that stage, in which process the activity of the catalysts in the two stages is varied so that the activity at the inlet end of each of the reaction tubes is less than 100% and increases steadily or stepwise to 100% at or before each outlet end, and the off-gas obtained at the outlet of the second reaction stage is substantially freed from condensable gases and recycled to the first stage as inert diluting gas, optionally together with steam.

The acrylic acid does not occur in an unduly dilute state, so that subsequent working up to pure acrylic acid requires considerably less time and energy. There was a prejudice against such measures, as one would have thought that the absolute yield would fall markedly on account of the dilution of the active catalyst composition. Surprisingly, this is not the case. The measures of the invention enable a system of the kind under consideration to be operated at substantially higher space velocities, which means that the throughput may be raised considerably without danger, the absolute yield obtained in the process of the invention being, as hitherto, about 50% on propylene introduced. Another advantage gained in diluting the catalyst is that when the synthesis gas is replaced by recycled reaction gases, which are known to have a sub-

stantially lower heat capacity than steam, the risk of overoxidation and local overheating is dispelled. The process of the invention constitutes a big economical improvement over conventional processes, since this second measure enables acrylic acid to be obtained in condensate concentrations of up to 50% by weight.

The process of the invention is carried out as follows:

Irrespective of any particular catalyst system, propylene concentrations of more than 2% molar based on the initial gaseous mixture (i.e. propylene plus molecular oxygen plus any other gas present) are used and the rate of flow of the propylene or acrolein (as the case may be) supplied to each stage is more than 60 liters of propylene per hour per liter of catalyst in that stage. Advantageously the bath temperatures used are those required for a propylene or acrolein conversion of more than 80% molar, preferably more than 85% molar.

The reaction of this gas mixture is carried out in the presence of catalysts the activity of which is varied, e.g. by dilution of the active composition with inert material. This variation is effected in such a manner that the activity of the catalyst which is initially less than 100% rises steadily or stepwise from the inlet end of the outlet end of the reaction tubes to reach a final value of 100%, which value is conveniently reached at some distance before the outlet end of the reaction tube. Advantageously, from 5 to 50% by weight of the total catalyst composition is diluted. Of particular industrial interest is a dilution of from 10 to 30% by weight. In other words, the activity of the catalyst preferably reaches 100% at a point upstream of the half-way point of the reaction tube. The amount of dilution in the diluted part of the catalyst bed for best results is dependent on the linear gas velocity. The amount of reduction of catalyst activity must be greater the higher the linear gas velocity, if the occurrence of uncontrollable hot spots is to be avoided. According to the present invention, at linear gas velocities of more than 60 cm/s (calculated for a reaction tube without packing), the activity of the catalyst, i.e. the proportion of active catalyst composition, in the diluted portion of the catalyst bed conveniently rises along the reaction tube from 0 to 100%. Advantageously, the initial dilution is such that the amount of active composition is from 25 to 75%, this being raised until it reaches 100%. The catalyst may be diluted with any material which is inert to the reaction, is stable at temperatures of at least 600° C and preferably at least 700° C, is substantially non-porous and does not combine with the components of the catalyst under the conditions of the reaction. Suitable materials are, for example, highly calcined oxides of aluminum, zirconium, titanium, magnesium

and silicon, the higher-melting silicates and aluminosilicates, electrode graphite, cement compositions, high-melting sintered compositions, preferably steatite,  $\alpha$ -alumina and silicon carbide.

5 Dilution is conveniently effected by mechanically mixing catalyst mouldings with mouldings of inert material of substantially the same shape or by mixing catalyst and inert material  
10 both in finely powdered form followed by shaping.

The reaction gases obtained at the end of the second reaction stage are freed from acrylic acid, steam and other condensible products  
15 by cooling and are mixed with the starting gas mixture entering the first reaction stage and mainly consisting of propylene, air and possibly steam, the mixing rate being such that, taking into consideration the unreacted propylene and  
20 the oxygen contained in the recycled off-gas, the total propylene concentration of the gas entering the first catalyst bed is more than 2% and preferably from 4 to 8% molar of the total gaseous mixture and, desirably, the molar ratios of propylene to oxygen and propylene to  
25 water are from 1:1.5 to 1:4, preferably 1:2 to 1:3, and from 1:0 to 1:3, preferably 1:0 to 1:2, respectively.

In the process of the invention the catalysts  
30 used in the first stage advantageously contain molybdenum, tungsten and tellurium in addition to oxygen, the atomic ratio of molybdenum to tungsten being from 0.03:1 to 40:1 and preferably from 0.2:1 to 25:1, and the content of tellurium being from 0.2 to 2% by  
35 weight and preferably from 0.5 to 1.8% by weight, and the catalysts used in the second stage advantageously contain molybdenum, tungsten and iron and/or nickel and/or manganese and/or copper in addition to oxygen  
40 and optionally vanadium, the atomic ratio of molybdenum to iron (nickel, manganese, copper) and tungsten to iron (nickel, manganese, copper) being from 1:1 to 20:1, preferably from 2:1 to 10:1, and from 0.01:1 to 10:1, preferably from 0.1:1 to 2:1, respectively, and the atomic ratio of molybdenum to vanadium being 6:0.2 to 6 and preferably  
45 6:0.5 to 4. Other catalysts suitable for the first and second stages of the process are those commonly used for the oxidation of propylene to acrolein or of acrolein to acrylic acid as described, for example, in German Printed Applications 1,924,496 and 2,000,425, Belgian  
50 Patents 689,720, 746,202 and 738,250, the published Dutch Patent Application 70.11603 and Japanese Patent Application 7,022,525 published in 1970.

The measures proposed by the invention  
60 make it possible to carry out the process at high throughputs of more than 100 liters of propylene (STP) per liter of catalyst per stage and linear gas velocities of more than 60 and

preferably more than 100 cm/s (STP) calculated for the reaction tube without packing,  
65 and bath temperatures associated with propylene conversions (first stage) and acrolein conversions (second stage) of more than 80% molar, preferably more than 85% molar, and with acrylic acid yields of more than 45—50%  
70 molar based on propylene introduced. These temperatures are dependent on the catalyst used but, generally speaking they are 280 to 450° C, preferably 310 to 400° C, for the first stage and 180 to 450° C, preferably 210  
75 to 350° C, for the second stage.

#### Comparative Examples A to H and Example 1.

The following Comparative Examples and Example clearly show that the space-time yield is approximately 2 to 3 times higher when the  
80 reaction gases are passed over a catalyst which is initially highly diluted and then shows a steady or stepwise increase in concentration in one stage (Comparative Example C) or in both stage in the manner proposed by the  
85 invention (Comparative Examples D—H) than when undiluted catalysts are used (Comparative Examples A—B). Although recycling of the off-gases or part thereof to the process (Example 1) to replace the steam according to  
90 the invention produces no further increase in the space-time yield, it does have the advantage of doubling the concentration of acrylic acid in the aqueous solution obtained.

The experiments were carried out as follows:  
95 A mixture of propylene (98%), air, steam and optionally nitrogen and containing 1.8% v/v of carbon monoxide was passed through a two-stage apparatus consisting of two series-connected steel tubes of 4 m in length and 25 mm in diameter. The tubes were in electrically  
100 heated, stirred salt baths. The gases entering the tubes were passed over heat exchangers to be preheated or cooled as necessary to reach the temperature of the particular salt bath. The reaction gas leaving the second stage at a temperature of from 200° to 300° C was cooled in a two-stage quencher system with the condensate produced. The catalyst packing  
105 used in the first stage was a molybdenum/tungsten tellurium catalyst, and in the second stage it was a molybdenum/tungsten/vanadium/iron catalyst, both catalysts being in the form of 3 × 3 mm pellets. The initial layers of the catalyst were diluted with  
110 steatite spheres having a diameter of 3 mm.

The following Table gives details of the amount of catalyst used, the degree of dilution, the gas rates, bath temperatures and conversions, acrylic acid yields, yields of residual  
115 acrolein at the end of the second stage (in each case based on the 98% propylene introduced to the first stage, the space-time yields and the condensate concentration of the acrylic acid product.

TABLE  
Examples 1 to 9

Example or Comparative Example	Catalyst Packing		Gas Rates (l/hr)				Bath Temp. for		Conversion of C <sub>3</sub> H <sub>6</sub> (% molar)	Yields of		Conc. of acrylic acid in condensate (% w/w)	
	tube I (ml)	tube 2 (ml)	C <sub>3</sub> H <sub>6</sub> air	H <sub>2</sub> O	N <sub>2</sub> /CO	tube I (°C)	tube II (°C)	acid (% molar)		acrolein (% molar)			
A	600 (100%+)	300 (100%+)	36	420	196	—	340	250	92	45	4	1.1	18 to
B	1000 (100%+)	500 (100%+)	60	720	336	—	340	250	88	30/40	3	1.2/1.8	20
C	400 (25%+)	500 (100%+)	60	720	336	—	325	260	94	55	1.6	2.2	
	900 (100%+)												
D	400 (25%+)	400 (25%+)	60	720	336	—	330	270	95	58	1.1	2.3	
	900 (100%+)	400 (100%+)											
E	400 (25%+)	400 (25%+)	90	1080	504	—	325	271	92	56	1.1	3.4	
	1100 (100%+)	500 (100%+)											
F	200 (25%+)	400 (25%+)	120	1440	660	—	342	255	94	60	1.5	5.6	24.5
	150 (33%+)	700 (100%+)											
	100 (50%+)												
	1050 (100%+)												
G	"	"	120	1440	390	—	330	256	89	53	1.3	4.4	30
H	120 (25%+)	120 (25%+)	120	1440	820	—	340	272	95	53	1.4	4.4	20.3
	210 (35%+)	210 (35%+)											
	140 (50%+)	140 (50%+)											
	1030 (100%+)	630 (100%+)											
I	"	"	120	1440	147	824	335	272	92	53	1.5	4.4	43.6

+ These percentages are percentages by volume of active composition

++ Space-time yield expressed as kg of acrylic acid per tube per day

## EXAMPLES 2 to 9.

Using catalysts manufactured by known methods, a mixture of fresh propylene, fresh air and recycle gas and containing 100 parts by volume per hour of propylene, 252 parts by volume per hour of oxygen, 50 parts by volume per hour of steam and 1,728 parts by volume per hour of inert gases (mainly nitrogen and small amounts of carbon oxides) is oxidised in two series-connected reaction tubes in two stages at the temperatures given in the following Table 2. The composition of the catalysts is given in Table 2. The catalysts used in the first stage have an activity of 25% over the first 0.091 parts by volume, as considered in the direction of flow of the gas mixture, an activity of 50% over the following 0.12 parts by volume and an activity of 100% over the

remaining 0.91 parts by volume; whilst the catalysts used in the second stage have an activity of 50% over the first 0.091 parts by volume and an activity of 100% over the remaining 0.73 parts by volume. The activity of the catalysts was reduced to the desired values by dilution with inert solids (steatite spheres of 3 mm in diameter). The catalysts themselves were in the form of 3 × 3 mm pellets. The recycled gas is off-gas from the second stage from which the condensable reaction products have been virtually completely washed out.

The following Table 2 lists the proportion of acrylic acid in the condensate, the yield of acrylic acid, the conversion of the propylene and the space-time yield of the acrylic acid in each case.

TABLE 2

Example	Catalyst		Bath Temp.		Acrylic acid in condensate (%w/w)	Converts. of $C_3H_6$ (mol %)	Yield of acrylic acid (mol %)	STY <sup>+</sup>
	Stage 1	Stage 2	Stage 1 (°C)	Stage 2 (°C)				
2	$Mo_{10}Ni_{7.5}Cr_1Fe_{0.33}Bi_{0.83}Sn_{0.5}$ on 30% $SiO_2$ (DOS 2,000,425; Ex. 1)	$Mo_6W_1V_1Fe_{1.5}$ (Belgian Patent 746,202)	362	260	52	91	52	4.0
3	"	$Mo_{12}V_{3.8}Sb_1$ on alumina pellets (DOS 2,038,763; Ex. 1)	390	420	39	76	39	3.0
4	$Mo_{10}Ni_{7.5}Cr_1Fe_{0.33}Bi_{0.83}Ge_1$ on 30% $SiO_2$ (DOS 2,000,425; Ex. 6)	$Mo_6W_1V_1Fe_{1.5}$ (Belgian Patent 746,202)	360	260	51	94	53	4.1
5	$Mo_{10}Ni_{10}Co_{0.3}Fe_1P_1Bi_1 + 1\%$ $Sn_2O_3$ on 33% Al-silicate (Belgian Patent 738,250; Ex. 1)	$Mo_6W_1V_1Fe_{1.5}$ (Belgian Patent 746,202)	390	260	50	79	50	3.9
6	$Mo_{10}Ni_1Co_3Fe_2Bi_1P_2K_{0.2}$ on 30% $SiO_2$ (DOS 2,020,791; Ex. 1)	$Mo_6W_1V_1Fe_{1.5}$ (Belgian Patent 746,202)	390	260	52	62	44	4.3
7	$Mo_7Ni_{10}Cr_2Te_{0.35}$	$Mo_6W_1V_1Fe_{1.5}$ (Belgian Patent 746,202)	400	270	47	79	38	2.9
8	$Mo_6W_8Te_{0.35}$ (British Patent 1,243,794)	$Mo_6W_1V_1Fe_{1.5}$ (Belgian Patent 746,202)	365	250	53	94	54	4.2
9	"	$Mo_{12}V_{3.8}Sb_1$ on alumina pellets (DOS 2,038,763; Ex. 1)	365	410	51	90	52	4.0

+ Space-time yield expressed in parts by weight of acrylic acid per tube per day

Comparative Example J (cf. Example 3).

The same apparatus is used as that employed in Examples 2 to 9 but in the first stage the catalyst used is 1.12 parts by volume of the catalyst given in Example 1 of German Printed Application DOS 2,000,425 and having an activity of 100%, whilst in the second stage the catalyst is 0.91 part by volume of the catalyst given in Example 1 of German Printed Application DOS 2,038,763 and having an activity of 100%. A gas mixture of 100 parts by volume per hour of propylene, 1,200 parts by volume per hour of air and 780 parts by volume per hour of steam is passed through the series-connected reaction tubes. The bath temperature for the first tube is 362° and for the second tube 410° C. The propylene conversion is 92% molar, the space-time yield is 1.9 parts by weight per tube per day and the yield of acrylic acid is 25% molar on propylene introduced. The acrylic acid is contained in the condensate in a concentration of

only 14% by weight.

WHAT WE CLAIM IS:—

1. A process for the manufacture of acrylic acid by two-stage oxidation of propylene with molecular oxygen in admixture with inert diluting gas in reaction tubes packed with catalyst, propylene being substantially oxidized to acrolein in the first stage and further oxidation to acrylic acid occurring in the second stage, the initial propylene concentration being above 2% molar based on the initial gaseous mixture and the rate of flow of the propylene or acrolein (as the case may be) supplied to each stage being greater than 60 liters per hour per liter of catalyst in that stage, wherein the activity of the catalysts in each of the two stages is varied so that the activity at the inlet end of each of the reaction tubes is less than 100% and increases steadily or stepwise to 100% at or before each outlet end, and the off-gas obtained at the outlet of the second reaction stage is substantially freed from condensable gases and recycled to the first stage and employed therein as inert diluting gas, optionally together with steam.

2. A process as claimed in claim 1 wherein the activity of the catalyst reaches 100% upstream of the half-way point of the reaction tubes.

3. A process as claimed in claim 1 or 2 wherein the catalyst at the inlet end of the reaction tubes is diluted so as to contain from 25 to 75% of active composition.

4. A process as claimed in any of claims 1 to 3 wherein the off-gases obtained at the outlet of the second reaction stage are mixed with propylene, air and optionally steam for the first reaction stage in amounts such that the resulting mixture contains more than 2% molar propylene and the molar ratios of propylene: oxygen and propylene: water therein are from 1:1.5 to 1:4 and from 1:0 to 1:3 respectively.

5. A process as claimed in any of claims 1 to 4 wherein the bath temperature used is that associated with a propylene or acrolein conversion of more than 80% molar.

6. A process as claimed in any of claims 1 to 5 wherein the linear gas velocity is more than 60 cm/sec (STP) calculated for the reaction tubes without packing.

7. A process as claimed in any of claims 1 to 6 wherein the first stage catalyst contains molybdenum, tungsten and tellurium in addition to oxygen and the second stage catalyst contains molybdenum, tungsten and one or more of iron, nickel, manganese and copper, in addition to oxygen and optionally vanadium.

8. A process for the manufacture of acrylic acid as claimed in claim 1 substantially as hereinbefore described and exemplified in any of the foregoing Examples 1 to 9.

9. Acrylic acid when manufactured by a process as claimed in any of claims 1 to 8.

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10 This invention relates to a process for the manufacture of acrylic acid by oxidation of propylene in two stages via acrolein as intermediate, using oxidic catalysts.

15 It is known to oxidize propylene to acrylic acid in the gas phase in the presence of molecular oxygen-containing gases and steam and at an elevated temperature in contact with solid catalysts in two stages. In the first stage, the propylene is mainly converted to acrolein, and the resulting gas mixture is passed to the second stage without separation of the acrolein, where it is oxidized to acrylic acid in contact with a second catalyst.

25 Catalyst systems already proposed for the first stage contain elements in groups IVa to VIa, VIII and IVb to VIIb. Of these catalyst systems, tellurium - containing catalysts (catalysts containing tellurium dioxide or telluric acid or catalysts which contain bismuth or antimony with or without phosphorus) are distinguished by their particularly high selectivity in the formation of acrolein at a relatively low temperature of the saltpetre bath usually used for this reaction. Other suitable catalysts include those containing oxides of molybdenum, tungsten and tellurium or the oxides of cobalt, molybdenum and tellurium. Other catalysts which have been proposed contain, for example, iron, tin, antimony, vanadium, or nickel, cobalt, iron, bismuth, phosphorus and molybdenum in addition to oxygen, optionally with additions of samarium oxide and tantalum oxide. The manufacture and use of the first mentioned catalyst systems for the oxidation of propylene to acrolein is described, for example, in British Patents 1,193,489 and 1,243,794.

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60 It is advantageous to use catalysts which contain, in addition to oxygen, molybdenum, tungsten and iron and/or nickel and/or manganese and/or copper and, optionally, vanadium. The manufacture of these catalysts and their use in the oxidation of acrolein to acrylic acid is described in British Patent 1,213,325 and Canadian Patent 868,940.

70 The ultimate object of the teachings given in said literature is to obtain acrylic acid in an absolute yield which is as high as possible on the propylene introduced, whilst other factors of significance in carrying out these processes are not considered to a desirable extent.

75 One of the most important criteria is the space-time yield and the concentration of the acrylic acid in the condensate obtained. Considerable difficulties have been encountered in attempts to obtain high space-time yields and high condensate concentrations in industrial apparatus. Industrial single-stage or multistage processes for the synthesis of acrylic acid by gas-phase oxidation in the prior art are only capable of removing the locally occurring heat of reaction with the rapidity necessary for high conversions in a single pass when very uneconomical measures are adopted. For example, it is necessary to use tubes of narrow cross-section or to operate at low temperatures and thus with small amounts of catalyst and low throughputs (linear gas velocities) and, moreover, the gas to be oxidized must be protected from explosive combustion at the catalysts or



at least from overoxidation leading to undesirable by-products by dilution with large amounts of steam (up to 40% by volume). Relatively good absolute yields of acrylic acid, which may be as high as 50% of theory or more based on propylene introduced, are obtained, but an uneconomically high energy input and high investment costs are incurred because it is necessary to use low space velocities (long residence times) and the resulting acrylic acid is obtained in very dilute aqueous solution.

It has thus been desirable to make the entire process more economical by improving the space-time yield whilst having recourse to the previously worked-out methods of obtaining high absolute yields in a single pass. The present invention seeks to provide a safe oxidation process in which over-oxidation of the kind mentioned above is minimized and explosive combustion processes are reliably obviated.

According to the present invention there is provided a process for the manufacture of acrylic acid by two-stage oxidation of propylene with molecular oxygen in admixture with inert diluting gas in reaction tubes packed with catalyst, propylene being substantially oxidized to acrolein in the first stage and further oxidation to acrylic acid occurring in the second stage, the initial propylene concentration being above 2% molar based on the initial gaseous mixture and the rate of flow of the propylene or acrolein (as the case may be) supplied to each stage being greater than 60 liters per hour per liter of catalyst in that stage, in which process the activity of the catalysts in the two stages is varied so that the activity at the inlet end of each of the reaction tubes is less than 100% and increases steadily or stepwise to 100% at or before each outlet end, and the off-gas obtained at the outlet of the second reaction stage is substantially freed from condensable gases and recycled to the first stage as inert diluting gas, optionally together with steam.

The acrylic acid does not occur in an unduly dilute state, so that subsequent working up to pure acrylic acid requires considerably less time and energy. There was a prejudice against such measures, as one would have thought that the absolute yield would fall markedly on account of the dilution of the active catalyst composition. Surprisingly, this is not the case. The measures of the invention enable a system of the kind under consideration to be operated at substantially higher space velocities, which means that the throughput may be raised considerably without danger, the absolute yield obtained in the process of the invention being, as hitherto, about 50% on propylene introduced. Another advantage gained in diluting the catalyst is that when the synthesis gas is replaced by recycled reaction gases, which are known to have a sub-

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The process of the invention is carried out as follows:

Irrespective of any particular catalyst system, propylene concentrations of more than 2% molar based on the initial gaseous mixture (i.e. propylene plus molecular oxygen plus any other gas present) are used and the rate of flow of the propylene or acrolein (as the case may be) supplied to each stage is more than 60 liters of propylene per hour per liter of catalyst in that stage. Advantageously the bath temperatures used are those required for a propylene or acrolein conversion of more than 80% molar, preferably more than 85% molar.

The reaction of this gas mixture is carried out in the presence of catalysts the activity of which is varied, e.g. by dilution of the active composition with inert material. This variation is effected in such a manner that the activity of the catalyst which is initially less than 100% rises steadily or stepwise from the inlet end of the outlet end of the reaction tubes to reach a final value of 100%, which value is conveniently reached at some distance before the outlet end of the reaction tube. Advantageously, from 5 to 50% by weight of the total catalyst composition is diluted. Of particular industrial interest is a dilution of from 10 to 30% by weight. In other words, the activity of the catalyst preferably reaches 100% at a point upstream of the half-way point of the reaction tube. The amount of dilution in the diluted part of the catalyst bed for best results is dependent on the linear gas velocity. The amount of reduction of catalyst activity must be greater the higher the linear gas velocity, if the occurrence of uncontrollable hot spots is to be avoided. According to the present invention, at linear gas velocities of more than 60 cm/s (calculated for a reaction tube without packing), the activity of the catalyst, i.e. the proportion of active catalyst composition, in the diluted portion of the catalyst bed conveniently rises along the reaction tube from 0 to 100%. Advantageously, the initial dilution is such that the amount of active composition is from 25 to 75%, this being raised until it reaches 100%. The catalyst may be diluted with any material which is inert to the reaction, is stable at temperatures of at least 600° C and preferably at least 700° C, is substantially non-porous and does not combine with the components of the catalyst under the conditions of the reaction. Suitable materials are, for example, highly calcined oxides of aluminum, zirconium, titanium, magnesium

and silicon, the higher-melting silicates and aluminosilicates, electrode graphite, cement compositions, high-melting sintered compositions, preferably steatite,  $\alpha$ -alumina and silicon carbide.

Dilution is conveniently effected by mechanically mixing catalyst mouldings with mouldings of inert material of substantially the same shape or by mixing catalyst and inert material both in finely powdered form followed by shaping.

The reaction gases obtained at the end of the second reaction stage are freed from acrylic acid, steam and other condensible products by cooling and are mixed with the starting gas mixture entering the first reaction stage and mainly consisting of propylene, air and possibly steam, the mixing rate being such that, taking into consideration the unreacted propylene and the oxygen contained in the recycled off-gas, the total propylene concentration of the gas entering the first catalyst bed is more than 2% and preferably from 4 to 8% molar of the total gaseous mixture and, desirably, the molar ratios of propylene to oxygen and propylene to water are from 1:1.5 to 1:4, preferably 1:2 to 1:3, and from 1:0 to 1:3, preferably 1:0 to 1:2, respectively.

In the process of the invention the catalysts used in the first stage advantageously contain molybdenum, tungsten and tellurium in addition to oxygen, the atomic ratio of molybdenum to tungsten being from 0.03:1 to 40:1 and preferably from 0.2:1 to 25:1, and the content of tellurium being from 0.2 to 2% by weight and preferably from 0.5 to 1.8% by weight, and the catalysts used in the second stage advantageously contain molybdenum, tungsten and iron and/or nickel and/or manganese and/or copper in addition to oxygen and optionally vanadium, the atomic ratio of molybdenum to iron (nickel, manganese, copper) and tungsten to iron (nickel, manganese, copper) being from 1:1 to 20:1, preferably from 2:1 to 10:1, and from 0.01:1 to 10:1, preferably from 0.1:1 to 2:1, respectively, and the atomic ratio of molybdenum to vanadium being 6:0.2 to 6 and preferably 6:0.5 to 4. Other catalysts suitable for the first and second stages of the process are those commonly used for the oxidation of propylene to acrolein or of acrolein to acrylic acid as described, for example, in German Printed Applications 1,924,496 and 2,000,425, Belgian Patents 689,720, 746,202 and 738,250, the published Dutch Patent Application 70.11603 and Japanese Patent Application 7,022,525 published in 1970.

The measures proposed by the invention make it possible to carry out the process at high throughputs of more than 100 liters of propylene (STP) per liter of catalyst per stage and linear gas velocities of more than 60 and

preferably more than 100 cm/s (STP) calculated for the reaction tube without packing, and bath temperatures associated with propylene conversions (first stage) and acrolein conversions (second stage) of more than 80% molar, preferably more than 85% molar, and with acrylic acid yields of more than 45—50% molar based on propylene introduced. These temperatures are dependent on the catalyst used but, generally speaking they are 280 to 450° C, preferably 310 to 400° C, for the first stage and 180 to 450° C, preferably 210 to 350° C, for the second stage.

Comparative Examples A to H and Example 1.

The following Comparative Examples and Example clearly show that the space-time yield is approximately 2 to 3 times higher when the reaction gases are passed over a catalyst which is initially highly diluted and then shows a steady or stepwise increase in concentration in one stage (Comparative Example C) or in both stage in the manner proposed by the invention (Comparative Examples D—H) than when undiluted catalysts are used (Comparative Examples A—B). Although recycling of the off-gases or part thereof to the process (Example 1) to replace the steam according to the invention produces no further increase in the space-time yield, it does have the advantage of doubling the concentration of acrylic acid in the aqueous solution obtained.

The experiments were carried out as follows: A mixture of propylene (98%), air, steam and optionally nitrogen and containing 1.8% v/v of carbon monoxide was passed through a two-stage apparatus consisting of two series-connected steel tubes of 4 m in length and 25 mm in diameter. The tubes were in electrically heated, stirred salt baths. The gases entering the tubes were passed over heat exchangers to be preheated or cooled as necessary to reach the temperature of the particular salt bath. The reaction gas leaving the second stage at a temperature of from 200° to 300° C was cooled in a two-stage quencher system with the condensate produced. The catalyst packing used in the first stage was a molybdenum/tungsten tellurium catalyst, and in the second stage it was a molybdenum/tungsten/vanadium/iron catalyst, both catalysts being in the form of 3 × 3 mm pellets. The initial layers of the catalyst were diluted with steatite spheres having a diameter of 3 mm.

The following Table gives details of the amount of catalyst used, the degree of dilution, the gas rates, bath temperatures and conversions, acrylic acid yields, yields of residual acrolein at the end of the second stage (in each case based on the 98% propylene introduced to the first stage, the space-time yields and the condensate concentration of the acrylic acid product.

TABLE  
Examples 1 to 9

Example or Comparative Example	Catalyst Packing		Gas Rates (1/hr)			Bath Temp. for Examples 1 to 9		Conversion of C <sub>3</sub> H <sub>6</sub> (% molar)	Yields of		Conc. of acrylic acid in condensate (% w/w)		
	tube I (ml)	tube 2 (ml)	C <sub>3</sub> H <sub>6</sub> air	H <sub>2</sub> O	N <sub>2</sub> /CO	tube I (°C)	tube II (°C)		acid (% molar)	acrolein (% molar)			
A	600 (100%+)	300 (100%+)	36	420	196	—	340	250	92	45	4	1.1	18 to
B	1000 (100%+)	500 (100%+)	60	720	336	—	340	250	88	30/40	3	1.2/1.8	20
C	400 (25%+)	500 (100%+)	60	720	336	—	325	260	94	55	1.6	2.2	
	900 (100%+)												
D	400 (25%+)	400 (25%+)	60	720	336	—	330	270	95	58	1.1	2.3	
	900 (100%+)	400 (100%+)											
E	400 (25%+)	400 (25%+)	90	1080	504	—	325	271	92	56	1.1	3.4	
	1100 (100%+)	500 (100%+)											
F	200 (25%+)	400 (25%+)	120	1440	660	—	342	255	94	60	1.5	5.6	24.5
	150 (33%+)	700 (100%+)											
	100 (50%+)												
	1050 (100%+)												
G	"	"	120	1440	390	—	330	256	89	53	1.3	4.4	30
H	120 (25%+)	120 (25%+)	120	1440	820	—	340	272	95	53	1.4	4.4	20.3
	210 (35%+)	210 (35%+)											
	140 (50%+)	140 (50%+)											
	1030 (100%+)	630 (100%+)											
I	"	"	120	1440	147	824	335	272	92	53	1.5	4.4	43.6

+ These percentages are percentages by volume of active composition

++ Space-time yield expressed as kg of acrylic acid per tube per day

## EXAMPLES 2 to 9.

Using catalysts manufactured by known methods, a mixture of fresh propylene, fresh air and recycle gas and containing 100 parts by volume per hour of propylene, 252 parts by volume per hour of oxygen, 50 parts by volume per hour of steam and 1,728 parts by volume per hour of inert gases (mainly nitrogen and small amounts of carbon oxides) is oxidised in two series-connected reaction tubes in two stages at the temperatures given in the following Table 2. The composition of the catalysts is given in Table 2. The catalysts used in the first stage have an activity of 25% over the first 0.091 parts by volume, as considered in the direction of flow of the gas mixture, an activity of 50% over the following 0.12 parts by volume and an activity of 100% over the

remaining 0.91 parts by volume; whilst the catalysts used in the second stage have an activity of 50% over the first 0.091 parts by volume and an activity of 100% over the remaining 0.73 parts by volume. The activity of the catalysts was reduced to the desired values by dilution with inert solids (steatite spheres of 3 mm in diameter). The catalysts themselves were in the form of 3 × 3 mm pellets. The recycled gas is off-gas from the second stage from which the condensable reaction products have been virtually completely washed out.

The following Table 2 lists the proportion of acrylic acid in the condensate, the yield of acrylic acid, the conversion of the propylene and the space-time yield of the acrylic acid in each case.

TABLE 2

Example	Catalyst		Bath Temp.		Acrylic acid in condensate (%w/w)	Convers. of $C_3H_6$ (mol %)	Yield of acrylic acid (mol %)	STY+
	Stage 1	Stage 2	Stage 1 ( $^{\circ}C$ )	Stage 2 ( $^{\circ}C$ )				
2	$Mo_{1.0}Ni_{7.5}Cr_{1.0}Fe_{0.33}Bi_{0.83}Sn_{0.5}$ on 30% $SiO_2$ (DOS 2,000,425; Ex. 1)	$Mo_6W_1V_1Fe_{1.5}$ (Belgian Patent 746,202)	362	260	52	91	52	4.0
3	" "	$Mo_{12}V_{3.8}Sb_1$ on alumina pellets (DOS 2,038,763; Ex. 1)	390	420	39	76	39	3.0
4	$Mo_{1.0}Ni_{7.5}Cr_{1.0}Fe_{0.33}Bi_{0.83}Ge_1$ on 30% $SiO_2$ (DOS 2,000,425; Ex. 6)	$Mo_6W_1V_1Fe_{1.5}$ (Belgian Patent 746,202)	360	260	51	94	53	4.1
5	$Mo_{1.0}Ni_{1.0}Co_{0.3}Fe_{1.0}P_1Bi_1 + 1\%$ $Sm_2O_3$ on 33% Al-silicate (Belgian Patent 738,250; Ex. 1)	$Mo_6W_1V_1Fe_{1.5}$ (Belgian Patent 746,202)	390	260	50	79	50	3.9
6	$Mo_{1.5}Ni_{1.0}Co_{0.3}Fe_{2.0}Bi_{1.0}P_{0.2}$ on 30% $SiO_2$ (DOS 2,020,791; Ex. 1)	$Mo_6W_1V_1Fe_{1.5}$ (Belgian Patent 746,202)	390	260	52	62	44	4.3
7	$Mo_{0.7}Ni_{0.7}Cr_{0.3}Te_{0.35}$	$Mo_6W_1V_1Fe_{1.5}$ (Belgian Patent 746,202)	400	270	47	79	38	2.9
8	$Mo_4W_8Te_{0.55}$ (British Patent 1,243,794)	$Mo_6W_1V_1Fe_{1.5}$ (Belgian Patent 746,202)	365	250	53	94	54	4.2
9	" "	$Mo_{12}V_{3.8}Sb_1$ on alumina pellets (DOS 2,038,763; Ex. 1)	365	410	51	90	52	4.0

+ Space-time yield expressed in parts by weight of acrylic acid per tube per day

Comparative Example J (cf. Example 3).

The same apparatus is used as that employed in Examples 2 to 9 but in the first stage the catalyst used is 1.12 parts by volume of the catalyst given in Example 1 of German Printed Application DOS 2,000,425 and having an activity of 100%, whilst in the second stage the catalyst is 0.91 part by volume of the catalyst given in Example 1 of German Printed Application DOS 2,038,763 and having an activity of 100%. A gas mixture of 100 parts by volume per hour of propylene, 1,200 parts by volume per hour of air and 780 parts by volume per hour of steam is passed through the series-connected reaction tubes. The bath temperature for the first tube is 362° and for the second tube 410° C. The propylene conversion is 92% molar, the space-time yield is 1.9 parts by weight per tube per day and the yield of acrylic acid is 25% molar on propylene introduced. The acrylic acid is contained in the condensate in a concentration of

only 14% by weight.

WHAT WE CLAIM IS:—

1. A process for the manufacture of acrylic acid by two-stage oxidation of propylene with molecular oxygen in admixture with inert diluting gas in reaction tubes packed with catalyst, propylene being substantially oxidized to acrolein in the first stage and further oxidation to acrylic acid occurring in the second stage, the initial propylene concentration being above 2% molar based on the initial gaseous mixture and the rate of flow of the propylene or acrolein (as the case may be) supplied to each stage being greater than 60 liters per hour per liter of catalyst in that stage, wherein the activity of the catalysts in each of the two stages is varied so that the activity at the inlet end of each of the reaction tubes is less than 100% and increases steadily or stepwise to 100% at or before each outlet end, and the off-gas obtained at the outlet of the second reaction stage is substantially freed from condensable gases and recycled to the first stage and employed therein as inert diluting gas, optionally together with steam.

2. A process as claimed in claim 1 wherein the activity of the catalyst reaches 100% upstream of the half-way point of the reaction tubes.

3. A process as claimed in claim 1 or 2 wherein the catalyst at the inlet end of the reaction tubes is diluted so as to contain from 25 to 75% of active composition.

4. A process as claimed in any of claims 1 to 3 wherein the off-gases obtained at the outlet of the second reaction stage are mixed with propylene, air and optionally steam for the first reaction stage in amounts such that the resulting mixture contains more than 2% molar propylene and the molar ratios of propylene: oxygen and propylene: water therein are from 1:1.5 to 1:4 and from 1:0 to 1:3 respectively.

5. A process as claimed in any of claims 1 to 4 wherein the bath temperature used is that associated with a propylene or acrolein conversion of more than 80% molar.

6. A process as claimed in any of claims 1 to 5 wherein the linear gas velocity is more than 60 cm/sec (STP) calculated for the reaction tubes without packing.

7. A process as claimed in any of claims 1 to 6 wherein the first stage catalyst contains molybdenum, tungsten and tellurium in addition to oxygen and the second stage catalyst contains molybdenum, tungsten and one or more of iron, nickel, manganese and copper, in addition to oxygen and optionally vanadium.

8. A process for the manufacture of acrylic acid as claimed in claim 1 substantially as hereinbefore described and exemplified in any of the foregoing Examples 1 to 9.

9. Acrylic acid when manufactured by a process as claimed in any of claims 1 to 8.

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